

REACTIVE MINERALS IN AQUIFERS: FORMATION PROCESSES AND QUANTITATIVE ANALYSIS

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Introduction

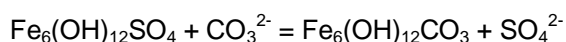
It is generally believed that biological processes dominate the attenuation mechanisms of volatile chlorinated organic compounds at contaminated sites. During biodegradation, this class of contaminants is ultimately transformed into innocuous byproducts such as carbon dioxide, chloride, methane, and water [e.g., 1]. Laboratory- and field-based evidence is emerging that suggests abiotic degradation processes play important roles in reducing contaminant concentration and mass [e.g., 2-7]. In particular, a variety of iron- and sulfur-bearing mineral species have been investigated in laboratory experiments. Reaction processes at the mineral-water interface appear to promote the rapid degradation of a variety of chlorinated compounds, including perchloroethylene (PCE) and trichloroethylene (TCE). Abiotic reaction conditions favor transformation of PCE and TCE by dichloroelimination rather than by sequential hydrogenolysis; consequently, this pathway is desirable in that the production of comparatively more toxic daughter products is circumvented.

There is a need to develop practical site characterization methodologies for decoupling the relative contributions of biotic and abiotic contaminant degradation. In addition, iron- and sulfur-bearing minerals are common corrosion products in zero-valent iron reactive barriers. Until recently, the formation of these corrosion products has been viewed as a process that limits the long-term performance of reactive barriers for groundwater cleanup. Yet some corrosion products that deposit on the surfaces of iron particles may also contribute to the overall treatment effectiveness of reactive barriers [e.g., 8]. In this presentation, the occurrence and form of selected reactive phases will be discussed, as well as available characterization methods that target these reactive minerals in aquifer materials and reactive barriers.

Reactive Iron Minerals

A variety of iron-bearing soil minerals have been studied as possible reactive materials for abiotic reductive dechlorination [e.g., 2-6]. Green rust, iron oxides (magnetite), and iron sulfides (disordered mackinawite, mackinawite, and pyrite) have been shown to support complete or nearly complete transformation of PCE, TCE and carbon tetrachloride. All of these minerals have been identified in aquatic environments, typically in iron-reducing and/or sulfate-reducing environments.

Green Rust – Green rust (GR) compounds are compositionally variable, mixed valence Fe(II)/Fe(III) layered hydroxides [9,10]. Green rust compounds have been identified in reducing soils and are common corrosion products in iron-based reactive barriers. Green rust structural units consist of alternating positively charged tri-octahedral metal hydroxide sheets and negatively charged interlayers of anions [11]. Anions present in the interlayer positions typically are Cl^- , CO_3^{2-} , or SO_4^{2-} . Two types of GR are distinguishable based upon X-ray diffraction analysis: GR1 in which the distance between hydroxide sheets is between about 0.75 and 0.80 nm (e.g., carbonate GR) and GR2 in which the distance between sheets is about 1.1 nm (e.g., sulfate GR). Solid-phase characterization and geochemical modeling studies of iron corrosion in Fe^0 permeable reactive barriers indicate that in non-mining impacted groundwater, carbonate forms of green rust precipitate preferentially over the sulfate form in zero-valent iron systems [8]. These observations can be understood by considering the following exchange equilibrium based upon the anhydrous GR components:



So that

$$K_1 = [\text{SO}_4^{2-} / \text{CO}_3^{2-}] \cdot [\text{Fe}_6(\text{OH})_{12}\text{CO}_3 / \text{Fe}_6(\text{OH})_{12}\text{SO}_4]$$

Assuming ideal mixing relations in the solids and taking available thermodynamic data [12], we estimate $K_1 = 10^{3.1}$. Typically the $[\text{SO}_4^{2-} / \text{CO}_3^{2-}]$ ratio in non-mining impacted groundwater is $<10^{3.1}$, consistent with the predominance in aquifers and most reactive barriers of carbonate GR over sulfate GR.

Iron Oxides – Magnetite (Fe_3O_4) is a comparatively dense mixed valence iron oxide. The structure of magnetite is that of an inverse spinel, which can be expressed by rewriting the formula as $\text{Fe}^{3+}(\text{Fe}^{2+}, \text{Fe}^{3+})\text{O}_4$. Magnetite may form in soils as a consequence of microbial or abiotic precipitation processes. Magnetite is also a common corrosion product in Fe^0 reactive barriers. In PRBs, magnetite appears to form as a transformation product of green rust.

Iron Sulfides – Transition metal sulfides (e.g., NiS , CuS , ZnS , CdS , HgS) have exceedingly low solubility products and might be expected to form in sulfate-reducing environments. However, with the exception of iron, transition metals are typically present in trace amounts in aquifer materials, which does not allow for any significant accumulation of sulfide minerals other than those of iron. Consequently, iron sulfides are the only metal sulfides commonly recognized in soils and sediments. In contaminated systems with high metal loadings, sulfides of Hg , Zn , Cd , and Cu have been reported.

Several iron sulfide phases have been synthesized in the laboratory, either as transient intermediates or as stable end products, and are therefore likely to form in subsurface environments. These phases are: disordered mackinawite, Fe_{1+x}S ; mackinawite, Fe_{1+x}S ; cubic iron sulfide, FeS ; hexagonal pyrrhotite, Fe_{1-x}S ; greigite, Fe_3S_4 ; smythite Fe_9S_{11} ; marcasite, orthorhombic FeS_2 ; and, pyrite, cubic FeS_2 . Pyrrhotite and pyrite represent the thermodynamically stable phases at the temperatures and pressures of early diagenesis. Disordered mackinawite, mackinawite, and greigite are metastable with respect to pyrite and/or stoichiometric pyrrhotite but are considered to be the principal precursor phases to pyrite [13].

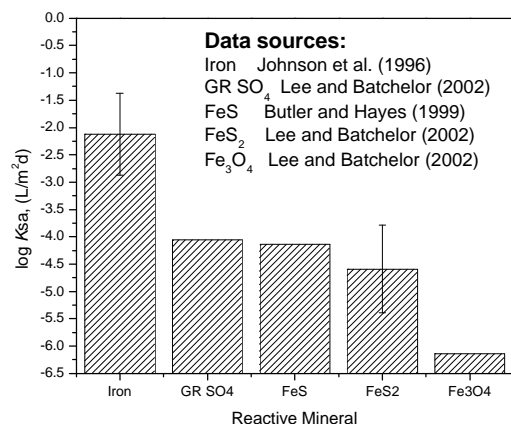


Figure 1. Surface area-normalized pseudo-first-order rate constants for the reductive dechlorination of TCE by iron metal, sulfate green rust, mackinawite, pyrite, and magnetite.

Reactivity and Stability – Surface area-normalized pseudo-first-order rate constants for the reductive dechlorination of TCE by iron metal and iron-bearing minerals have been compiled from indicated literature sources in Fig. 1. The trends present in this figure suggest that iron minerals potentially support fast reductive dechlorination and that more thermodynamically stable phases pyrite and magnetite support comparatively slower TCE reduction than precursor phases, green rust and mackinawite.

H_2 -pH diagrams showing the equilibrium relations in the system $\text{Fe-H}_2\text{O-C-S}$ are shown in Fig. 1A and 1B. These redox-pH diagrams were constructed with the EQ/36 thermodynamic database, modified to include data for green rust, iron sulfides, and iron metal. The diagrams show predominance areas for aqueous species (dashed lines) and solid phases (bold lines). Stability fields for siderite and the carbonate form of green rust are present in systems containing inorganic carbon. At the specified conditions, green rust appears to be a stable phase and not metastable as is sometimes assumed, i.e., no mineral phases were suppressed in order for green rust to appear on the Fig. 2A. When sulfur is exchanged for carbon, a broad stability field for pyrite (FeS_2) appears at low redox potentials, i.e., high hydrogen concentrations (Fig. 1B).

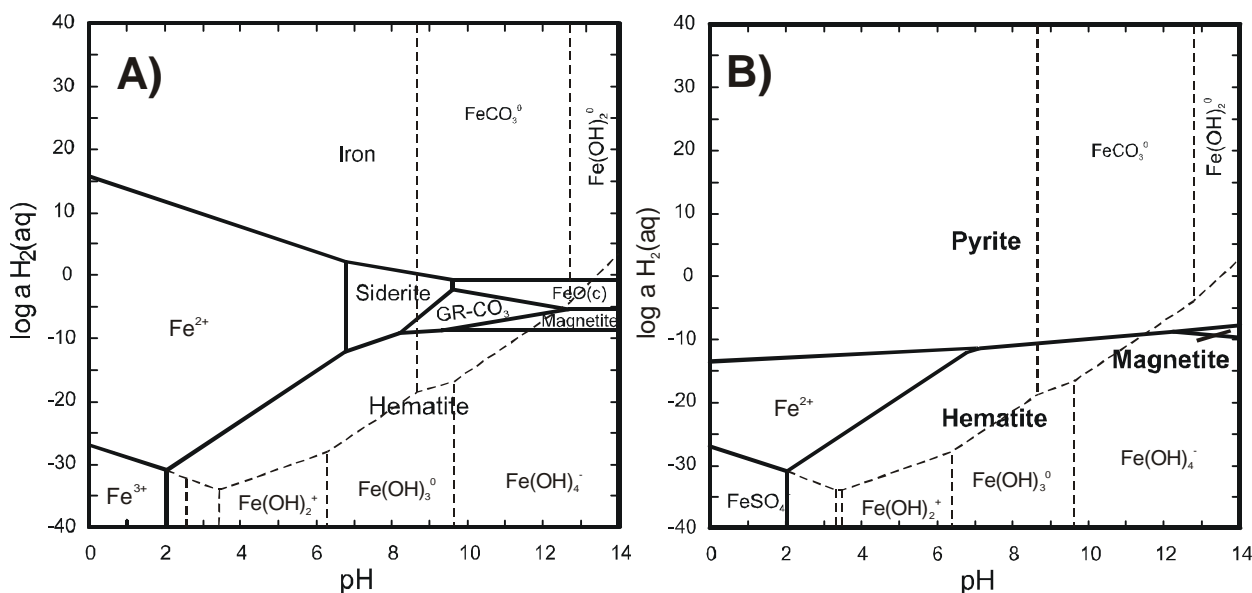


Figure 2. Log activity H_2 -pH diagram showing stability regions for dissolved species (dashed lines) and minerals (bold lines). **A)** Fe-C- H_2O system (25°C, $\Sigma C=10^{-2}$, $\Sigma Fe=10^{-5}$); **B)** Fe-S- H_2O system (25°C, $\Sigma S=10^{-3}$, $\Sigma Fe=10^{-5}$).

Characterization Methods

In order to access the importance of abiotic attenuation processes at contaminated sites sensitive mineralogical characterization is needed. A recent description of methods for determination of mineralogy and environmental availability may be found in ref. [15]. Characterization challenges related to the detection and measurement of iron-bearing phases discussed here includes redox sensitivity during sample collection and sample handling and accurate quantitation at low concentration levels. The essential components of solid-phase characterization studies specific to iron and sulfur compounds will include sample collection, sample fractionation (e.g., size or magnetic fractionation), determination of bulk elemental composition (e.g., total Fe and S), determination of mineralogy, and determination of element partitioning. These issues will reviewed in the presentation.

The process of collecting, storing, and handling materials prior to characterization is critical. Minerals containing ferrous iron and sulfide are typically sensitive to air exposure. Freezing of materials and storage under oxygen-free conditions will generally minimize the oxidation of redox-sensitive minerals. Size separation and magnetic separation can be particularly useful to isolate reactive minerals in aquifer materials; however, it must be emphasized that fractionation procedures need to be carried out under an anaerobic atmosphere to prevent oxidation.

X-ray diffraction is generally the most appropriate method for mineral identification among iron and sulfur phases. Detection limits will vary depending on the sample matrix and on the degree of crystallinity, but quantitation limits of about 1 to 5 wt% may be achieved for a given phase without preconcentration. Other possible methods for identifying iron minerals include Mössbauer spectroscopy (especially important for green rust), infrared spectrometry, thermal analysis, and the emerging synchrotron methods.

Chemical extraction methods are perhaps the most frequently used techniques for establishing iron and sulfur partitioning in sediments and soils. Methods designed to speciate among iron minerals typically involve complexation and protonation reactions. Hydrochloric acid, oxalic acid, ascorbic acid, and buffered sodium dithionite solutions are often used [e.g., 16]. Methods for partitioning sulfur among organic, acid-volatile sulfides (e.g., mackinawite), and chromium-reducible sulfur (e.g., pyrite and sulfur) are well established and sensitivity to 0.01 wt% is achievable for most sample types [e.g., 17,18].

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